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Temperature Dependence of Graphene and N-doped Graphene for Gas Sensor Applications

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Abstract

We report the response of graphene and N-doped graphene to ethanol vapor as gas sensors with varying the concentration of ethanol and temperature of graphene. Graphene was synthesized by chemical vapor deposition on copper foils and then was transferred to a glass slide by chemical etching. N-doped graphene was produced by annealing graphene in ammonia atmosphere. Results showed the response of both graphene and N-doped graphene are at low level up to 2.4%. The response of graphene increases with temperature up to 1.15%, but that of N-doped graphene decreases from down to 0.30%. We proposed the absorbed oxygen and nitrogen detachment are the key factors for the temperature dependence of the response of graphene and N-doped graphene, respectively.

1. Introduction

The metal oxide semiconductors were used widely for gas sensing because of their high response to numerous gas species with low production costs. Nanostructures of the narrow band gap metal oxide semiconductors were employed to enhance detection performance of sensors, for examples, CuO [1] and ZnO nanowires [2]. However, their drawbacks are selectivity and stability [3]. Graphene has many properties exceeding metal oxide semiconductor- based gas sensing, such as high surface area, high conductance, a high signal- to- noise ratio at low- level changing of local charge concentration [3]. Here, we investigate the response of graphene and N-doped graphene for varying concentrations of ethanol vapors and temperatures. N-doped graphene and graphene were prepared by chemical vapor deposition using acetylene as a carbon source. The response of sensors to ethanol was measured and derived for each condition. To investigate effects of sensor measurement, Raman spectroscopy and X-ray photoemission spectroscopy were utilized for characterization of samples before and after sensor measurement of ethanol vapors.

2. Experimental details

2.1 Graphene synthesis and nitrogen doping of graphene

Graphene was synthesized by chemical vapor deposition (CVD) on 1 cm x 1 cm of copper foils using acetylene. Details of CVD were described in our previous report [4]. Multilayer graphene was obtained on the both sides of the copper substrates. Then, graphene was transferred onto a glass substrate by chemical etching. This transferring procedure involves two-step etching method using nitric acid (NHO₃) and iron (III) nitrate (Fe(NO₃)₃). Graphene can be doped with nitrogen atoms by annealing graphene at 400 °C for 45 min under ammonia atmosphere [5].

2.2 Characterization and gas sensor measurement

As- grown graphene and N- doped graphene were characterized by Raman spectroscopy with an excitation wavelength of 532 nm by an HORIBA Jobin-Yvon T64000 Raman spectrometer and an AXIS ULTRA^{DLD} X-ray photoelectron spectroscopy (XPS) from Kratos analytical, UK. For sensor measurement, two electrodes were fabricated on samples by gold sputtering with SPI-Module Sputter Coater in the low vacuum for 120 seconds. Measurement of ethanol vapor was operated by applying voltage via the electrodes on the samples with Agilent 34970A and measure electrical current across the electrodes with Keithley196. The ethanol gas sensing was examined on graphene and N-doped graphene samples by ethanol vapor concentrations of 25, 50, 100 and 200 ppm for working time of 60 seconds at varying temperatures at 25, 100 and 150 °C.

3. Results and discussion

3.1 Characterization results

Raman spectrum of graphene sample before measuring ethanol vapor displayed in figure 1(A) (red). It contains three peaks at 1333, 1575 and 2654 cm⁻¹, which are assigned to D, G, and 2D respectively. Raman spectrum of graphene after measuring ethanol vapor (blue) at a concentration of 200 ppm at 150 °C have prominent peaks at 1335, 1584 and 2665 cm⁻¹, respectively. The Raman spectrum of graphene after measuring exhibits blue shift. The blue shift is attributed from compressive stress on graphene from annealing during graphene was heated [6]. For Raman spectrum of Ndoped graphene in figure 1(B), the red shift of the sample after measuring comparing to one before measuring was observed. This effect is attributed from a strain in graphene from nitrogen doping into graphene [7].



Figure.1 Raman spectra of (A) graphene and (B) N-doped graphene. Blue spectra are the sample before sensor operations and red spectra are after sensor operations.

กมยนต Graphene and N-doped graphene were analyzed by XPS to investigate the evolution of element composition of the samples before and after measuring ethanol for concentration of 200 ppm at 150 °C. Figure 2(A) shows XPS of N 1s for graphene before sensor examination. Two component peaks were given at 400.2 and 401.2 eV corresponding to pyrrolic-N and quaternary-N, respectively. These component bondings disappear after ethanol vapors measurement. We suggest chemical etching in transferring process was attributed to nitrogen doping into graphene and heating samples during ethanol vapor measurement would make desorption of nitrogen from graphene. Figure 2(B) displays devolution peaks of N-doped graphene in before measuring ethanol at 398.3, 399.3, 400.2 eV corresponding to pyrrolic-N bonds and at 401, 401.9 eV corresponding to quaternary-N bonds [4, 8-11]. Less component nitrogen peaks and quantity of nitrogen after measurement than before gas measurement was found. Fig.2(C) and (D) show O1s spectra of graphene and N-doped graphene. Quantity of oxygen after ethanol vapor measurement increases for graphene and N-doped graphene. It was explained by oxygen in ambient atmosphere and oxygen component in ethanol molecules at elevated temperature interacts and makes bonding with defect sites and nitrogen in graphene and N-doped graphene.

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Figure. 2 The XPS of N1s core level of (A) graphene and (B) N-doped graphene of N1s and XPS of O1s core level of (C) graphene and (D) N-doped graphene before and after measuring ethanol vapor.

3.2 Gas sensor measurement

The response to ethanol vapor was calculated by the ratio of the resistance of samples under an air atmosphere (R_a) to ethanol atmosphere (R_g). Results from the graphene sample at all temperatures show a low level of responsitivity ~1% with ethanol vapors in all concentrations. Figure 3 shows the response of samples to different ethanol vapor concentrations at varying temperatures. The response was defined as the following equation,

Response (%) =
$$\frac{\left|R_a - R_g\right|}{R_a} \times 100\%$$
 (1)

The response of graphene increases with temperature for most ethanol vapor concentrations except 50 and 100 ppm at 150 °C as displayed in figure 3 (A). The range of response for graphene is 0.07 to 1.19 %. Conversely, the response of N-doped graphene decreases with temperature shown in figure 3 (B). The response of N-doped graphene is from 0.30 to 2.34%. The highest response of 2.34% for N-doped graphene occurs for measuring at room temperature. No dependence of response to ethanol vapor was found.



Figure.3 Response of (A) graphene and (B) N-doped graphene at different operating temperatures for varying ethanol vapor concentrations.

3.3 Discussion

From the results of element analyzing and response of graphene and N-doped graphene, we proposed adsorbed oxygen in graphene surface is the main factor to govern temperature dependence of the response of graphene. Then, these adsorbed oxygen molecules in graphene were ionized and trapped electrons from the conduction band [12]. According to adsorption of oxygen, we can explain the ethanol vapor response of graphene in term of oxygen ions as shown in equation (2) [13],

$$6O_{2abs}^{-} + CH_3CH_2OH \rightarrow 2CO_2 + 3H_2O + S + 6e_{free}^{-}$$
 (2).

The reaction produces free electrons in graphene, resulting in decrease resistance of sensor samples [14]. The adsorbed oxygen ions in graphene will prevent ethanol molecules to have reactions with graphene surface. Therefore, at higher temperatures the rate of the reaction increase, leading to decrease of resistance and increase of response [14].

For N-doped graphene, we suggest ethanol vapor sensing process follows a different mechanism for understanding the decrease of response. Nitrogen in N-doped graphene provides free electrons and thus give the high mobility of electrons in graphene at room temperature. At elevated temperatures, the detachment of nitrogen from graphene structure occurs. It is evident from the decrease of nitrogen concentration in XPS results [15]. The raising temperature would either decrease the number of free electrons from nitrogen dopants or reduce electron mobility [16]. It can cause the high resistance of N-doped graphene for sensor measurement above room temperature, resulting in lower response.

4. Conclusions

Graphene and N-doped graphene were successfully synthesized by chemical vapor deposition. Responses of graphene and N-doped graphene to ethanol vapor were measured for varying ethanol vapor concentrations and at different temperatures. Temperature dependence of response was found. The response of graphene increases for increase temperature in sensor measurement, but that of N-doped graphene decreases. We suggest adsorbed oxygen on graphene can reduce free electrons causing a decrease of response. For N-doped graphene, nitrogen detachment from N-doped graphene leads to high resistance of N-doped graphene comparing to graphene, resulting in a decrease of response.

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